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Influence of dissolution/precipitation reactions on metamorphic greenschist to amphibolite-facies mica $^{40}\text{Ar}/^{39}\text{Ar}$ ages in the Longmen Shan (eastern Tibet)

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ABSTRACT

Linking ages to metamorphic stages in rocks that have experienced low to medium-grade metamorphism can be particularly tricky due to the rarity of index minerals and the preservation of mineral or compositional relicts. The timing of metamorphism and the Mesozoic exhumation of the metasedimentary units and crystalline basement that form the internal part of the Longmen Shan (eastern Tibet, Sichuan, China), is, for these reasons, still largely unconstrained, but crucial for understanding the regional tectonic evolution of the eastern Tibet. *In-situ* core-rim $^{40}\text{Ar}/^{39}\text{Ar}$ biotite and U-Th/Pb allanite data show that amphibolite-facies conditions (~10-11 kbar, 530 °C to 6-7 kbar, 580 °C) were reached at 210-180 Ma and that biotite records crystallization, rather than cooling, ages. These conditions are mainly recorded in the metasedimentary cover. The $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained from matrix muscovite that partially re-equilibrated during the post peak-*P* metamorphic history comprise a mixture of ages between that of early prograde muscovite relicts and the timing of late muscovite recrystallization at *c.* 140-120 Ma. This event marks a previously poorly documented greenschist facies metamorphic overprint. This latest stage is also recorded in the crystalline basement, and defines the timing of the greenschist-overprint (7 ± 1 kbar, 370 ± 35 °C). Numerical models of Ar diffusion show that the difference between $^{40}\text{Ar}/^{39}\text{Ar}$ biotite and muscovite ages cannot be explained by a slow and protracted cooling in an open system. The model and petrological results rather suggest that biotite and muscovite experienced different Ar retention and resetting histories. The Ar record in mica of the studied low to medium grade rocks seems to be mainly controlled by dissolution-precipitation processes rather than by diffusive loss, and by different microstructural positions in the sample. Together, our data show that the metasedimentary cover was

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thickened and cooled independently from the basement prior to *c.* 140 Ma (with a relatively fast cooling at 4.5 ± 0.5 °C/Ma between 185 and 140 Ma). Since the Lower Cretaceous the metasedimentary cover and the crystalline basement experienced a coherent history during which both were partially exhumed. The Mesozoic history of the Eastern border of the Tibetan plateau is therefore complex, polyphase, and the basement was actively involved at least since the Early Cretaceous, changing our perspective on the contribution of the Cenozoic geology.

Key words: $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, U-Th/Pb allanite geochronology, compositional mapping, greenschist-amphibolite-facies metamorphism, Longmen Shan

1 | INTRODUCTION

One of the major contributions to the understanding of the tectonic evolution of orogenic belts is the quantification of the rates of different parts of the burial and exhumation cycle experienced by the rocks now cropping out at the surface. However, in low to medium grade metamorphic terranes that have experienced multiple stages of metamorphism, distinguishing between, and dating, the different metamorphic event(s) can be challenging. Difficulties mainly derive from the significant mineral, compositional and microstructural inheritance preserved in the samples at relatively low temperatures.

Modern analytical instrumentation allows the structural complexity and chemical heterogeneity of low grade metamorphic minerals to be imaged and quantified with high precision (at the scale of 1-10 μm), especially in mica-bearing systems (e.g. Lanari et al., 2012, Lanari et al., 2013, Lanari et al., 2014a, Scheffer et al., 2016). In such systems, the $^{40}\text{Ar}/^{39}\text{Ar}$ dating of mica is commonly used to determine the timing of metamorphic cooling following the traditional interpretation of the Dodson's diffusion theory (Dodson, 1973), due to the ubiquity of mica and its importance as a geobarometer. However, the concentration of Ar incorporated in, or lost from a grain is not only dependent on the cooling history and the grain size (as suggested by the Dodson, 1973 formulation) but also on the effectiveness of the grain boundary fluid network in removing Ar (the 'openness' of the system) and the variation of the rates of fluid-induced replacement mineral reactions (de Sigoyer et al., 2000; Di Vincenzo, Ghiribelli, Giorgetti, & Palmeri, 2001; Mulch & Cosca, 2004; Villa, 2010; Warre, Hanke, & Kelley, 2012a; Warren, Smye, Kelley, & Sherlock, 2012b; Cenki-Tok, Darling, Rolland, Dhuime, & Storey, 2014; Fornash, Cosca, & Whitney, 2016; Villa, 2016).

Therefore, since many tectonic timescale estimates rely on the interpretation of metamorphic ages (Sanchez et al., 2011; Lanari et al., 2014c) and associated cooling rates (e.g. Mulch, Cosca, Andersen, & Fiebig, 2005; Rolland, Sosson, Adamia, & Sadradze, 2011), an integrated petrological and geochronological approach is necessary to precisely assess age significance within the geological context (Allaz, Engi, Berger, & Villa, 2011; Villa, Bucher, Bousquet, Kleinhanns, & Schmid, 2014; Villa, 2016). In complex cases, $^{40}\text{Ar}/^{39}\text{Ar}$ data may be combined with data from independent geochronometers (e.g. U-Th/Pb on zircon, monazite, allanite) and with results from numerical diffusion models to provide a means for distinguishing whether Ar age variations derive purely from Ar diffusion—thus providing constraints on cooling rates—or whether they derive from mineral recrystallization reactions during metamorphism (Mulch & Cosca, 2004; Cenki-Tok et al., 2014).

In the low to medium grade metamorphic rocks of the central Longmen Shan (eastern Tibetan plateau, Figure 1), petrological studies have documented a complex pattern of chemical heterogeneities within the metamorphic minerals, in particular within matrix white mica, relating to different phases of deformation and chemical re-equilibration events (Worley & Wilson, 1996; Airaghi, Lanari, de Sigoyer, & Guillot, 2017a; Airaghi et al.,

2017b). Field structures provide evidence for two successive compressional events: the first linked to the Late Triassic - Early Jurassic orogeny related to the closure of the Paleotethys, and coeval with granite emplacement from 224 to 188 Ma (Chen & Wilson, 1995; Roger, Malavieille, Leloup, Calassou, & Xu, 2004; Harrowfield & Wilson, 2005; Roger, Jolivet, & Malavieille, 2010; Yan, Zhou, Li, & Wei, 2011; de Sigoyer, Vanderhaeghe, Duchene, & Billerot, 2014), the second linked to the Cenozoic re-activation starting in the Eocene after the India-Asia collision (e.g. Arne et al., 1997; Wang et al., 2012). This latter event includes a period of rapid exhumation of the Longmen Shan crystalline units from *c.* 10 Ma, as demonstrated by U-Th/He apatite and zircon fission track ages (Kirby et al., 2002; Richardson et al., 2008; Godard et al., 2009; Wang et al., 2012; Li et al., 2012; Li, Currie, Rowley, & Ingalls, 2015; Tan, Lee, Xu, & Cook, 2017). A period of tectonic quiescence and slow cooling at rates of ~ 1 °C/Ma has been proposed between the two deformation phases (e.g. Roger, Jolivet, Cattin, & Malavieille, 2011). This suggestion was recently called into question by new $^{40}\text{Ar}/^{39}\text{Ar}$ ages that appear to document the re-activation of the crystalline Pengguan massif under greenschist facies conditions at *c.* 137 Ma, during the Early Cretaceous (Airaghi et al., 2017b).

In the internal domain of the belt (the area located west of the Wenchuan Fault, WF in Figure 1a-c), rocks record three stages of a clockwise metamorphic path: two stages of amphibolite-facies metamorphism related to the thickening of the sedimentary series and to the beginning of their exhumation (Worley & Wilson, 1996; Airaghi et al., 2017a). These stages are also observed in the Danba area (southeast of the Longmen Shan) at higher metamorphic conditions (Huang, Maas, Buick, & Williams, 2003; Weller et al., 2013; Jolivet, Roger, Xu, Paquette, & Cao, 2015; Billerot, Duchene, Vanderhaeghe, & de Sigoyer, 2017). Amphibolite-facies metamorphism was then followed by a greenschist-facies overprint (Dirks, Wilson, Chen, Luo, & Liu, 1994; Airaghi et al., 2017a). This complex tectono-metamorphic history and the relatively low metamorphic grade of the rocks make the geochronological estimations of the different metamorphic events particularly challenging. *In-situ* U-Pb monazite ages obtained from the metasedimentary cover in the Danba area (Figure 1a) bracket the medium-grade metamorphic history between 190 and 180 Ma (e.g. Weller et al., 2013). In the Longmen Shan, whether major metamorphic minerals such as biotite and muscovite, used for thermobarometric estimates record similar metamorphic events, still remains largely unconstrained. The timing and conditions of the greenschist facies overprint is also still unclear. In this study we report a new dataset of *in-situ* metamorphic biotite and muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ ages for the internal domain of the Longmen Shan (Figure 1b,c) to provide the first petro-chronological set of data for the belt and to date the greenschist overprint.

In-situ $^{40}\text{Ar}/^{39}\text{Ar}$ dating was carried to ensure the best spatial resolution possible in order to date minerals in different microstructural sites. Considering their close chemical composition, it would not be easy to discriminate between mica generations by standard step heating techniques. In order to strengthen age interpretation and decipher the major process controlling the $^{40}\text{Ar}/^{39}\text{Ar}$ record, *in-situ* dating was combined with (i) previously-reported and newly acquired compositional mapping, microstructural observations and *P-T* paths to put ages into a petro-structural context, (ii) allanite (REE-rich epidote) U-Th/Pb ages used as an independent chronometer, and (iii) simple diffusion models to explore the effect of different cooling paths and rates on $^{40}\text{Ar}/^{39}\text{Ar}$ ages.

This study provides new time constraints on the timescales of metamorphic processes in the internal domain of the central Longmen Shan and in the eastern Tibet in general during the Mesozoic, revealing a previously poorly documented Early Cretaceous phase. Furthermore, our results provide important insights on the petrological processes that control

different $^{40}\text{Ar}/^{39}\text{Ar}$ signatures in muscovite and biotite in low to medium grade metamorphic samples.

2 | GEOLOGICAL SETTING

The Longmen Shan range is located at the eastern border of the Tibetan plateau, between the Songpan Ganze block to the west and the Sichuan basin (South China craton) to the east (Figure 1a). From east to west (from the frontal to the internal part of the belt) three faults strike parallel to the belt: the Guanxian, the Beichuan and the Wenchuan faults that lie in the ductile Wenchuan Shear Zone (Figure 1a). The Neoproterozoic South China Craton crops out in the Pengguan and Xuelongbao crystalline massifs, in the hanging wall of the Beichuan and Wenchuan faults respectively (Zhou, Yan, Wang, Qi, & Kennedy, 2006; Yan et al., 2008). In the hanging wall of the Wenchuan fault, the Tonghua crystalline massif also crops out as a 75 km long slice of metagranitic and metagranodioritic rocks (Figure 1b,c) and is considered here to also belong to the South China Craton, due to its petrological characteristics and its association with the Neoproterozoic sedimentary roof ('Sinian' in Figure 1b).

The Tonghua massif is bounded to the northeast by a tectonic contact that separates it from the medium-grade metamorphosed Palaeozoic-Mesozoic sedimentary cover, structurally above the basement (Figure 1b,c). The metasedimentary cover mainly includes deformed Silurian metapelites and Devonian metagreywackes (Figure 1b,c). The Tonghua massif is folded, as demonstrated by the occurrence of the Neoproterozoic (Sinian) sedimentary rocks at both sides of the massif (Figure 1b,c). Close to the Wenchuan fault, the crystalline rocks are deformed under brittle-ductile conditions. Deformation is defined by northwest-dipping cleavage, cm-scale shear zones and veins where the basement is metamorphosed under greenschist-facies conditions, with assemblages of chlorite+white mica+epidote+quartz.

In the Tonghua and Pengguan crystalline massifs the greenschist-facies metamorphism is the major metamorphic overprint observed. No clear evidence of a higher-grade metamorphic history has been identified, in agreement with petrological observations on other crystalline massifs in the belt (e.g. Airaghi et al., 2017b). In the sedimentary cover of the Tonghua massif, an amphibolite-facies assemblage characterized by garnet and biotite (\pm allanite) has been overprinted by a later greenschist assemblage (Dirks et al., 1994; Worley & Wilson, 1996; Airaghi et al., 2017a). The geographical proximity of these different metamorphic domains poses questions regarding the timing of their juxtaposition as well as the difference between the metamorphic conditions of the metasedimentary cover and the crystalline massifs. For this study, a series of samples was collected: (i) in the lower structural levels of the pelitic metasedimentary cover exhumed in the hanging wall of the WF at a similar distance from the WF (samples to13-4, to13-5, to13-7, lm09-220 of Figures 1b and 2), (ii) in the upper crustal level of the same series (sample lm147) 35 km northeast from the WF and (iii) in the Tonghua crystalline massif, close to the WF (samples lm09-52, lm09-53 and to13-12 of Figures 1b and 3, see also Table 1 for sample location), in order to identify possible differences in the petro-chronological evolutions of different units.

3 | SAMPLE DESCRIPTION AND THERMOBAROMETRY

3.1 | Methods

Major minerals and allanite grains were identified on polished thin sections using optical microscopy and backscatter images performed with a Scanning Electron Microscope S2500 Hitachi at Institut des Sciences de la Terre (ISTerre - University Grenoble Alps, France; Figures 2, 3 and 4). The chemistry of the major minerals was analyzed with an Electron Probe Micro-analyzer (EPMA) JEOL JXA-8230 at ISTERRE. Point analyses were acquired using 15 keV accelerating voltage and 12 nA beam current with a beam size between 1 and 3 μm . Representative mineral compositions are shown in Table 2. In order to track the

chemical heterogeneity within the major minerals and allanite, X-ray maps of major minerals and allanite were acquired at 15 keV and 100 nA, a dwell time of 200 ms (300 ms for allanite) and were standardized using the program XMAPTOOLS 2.3.1 (Lanari et al. 2014a). The mineral compositions of samples to13-4 and to13-7 are recorded in detail by Airaghi et al. (2017a).

Garnet-biotite thermometry calculations were applied to sample to13-5 where garnet and biotite were observed in textural equilibrium, using the calibrations of Perchuk and Lavrent'eva (1983), Thompson (1976) and Holdaway and Lee (1977), at 10 kbar. The maximum temperature experienced by sample lm147 (T_{peak}) was estimated by Raman Spectroscopy on Carbonaceous Material (RSCM) following the procedure described by Beyssac, Rouzaud, Goffé, Brunet, and Chopin (2002), as no garnet was observed in this sample. *P-T* conditions of the greenschist assemblage in the samples from the crystalline Tonghua massif were estimated with the multi-equilibrium chlorite-white mica-quartz-H₂O thermobarometry, following the procedures described in Dubacq, Vidal, and De Andrade (2010), Lanari et al. (2012) and Airaghi et al. (2017b). Metamorphic conditions of the analyzed samples are reported in Table 1.

3.2 | Metasedimentary rocks

Samples collected in the Silurian to Devonian metasedimentary series (to13-4, to13-5, to13-7, lm09-220 and lm147) are metapelites metamorphosed under amphibolite-facies conditions, with assemblages of quartz+white mica+chlorite+garnet (except lm147) +biotite+ilmenite+feldspar (albite) and accessory apatite+allanite (\pm monazite, Figures 2 and 3).

The relative chronological evolution of microstructures and mineral growth observed at the outcrop and thin section scales is summarized in Figure 2a. Samples to13-4, to13-7 (described in detail by Airaghi et al., 2017a) and lm147 preserve an early white mica+chlorite-bearing S1 cleavage (related to the D1 phase of deformation). S1 is folded by a second S2 white mica-bearing crenulation cleavage associated with the D2 deformation (Figure 2b-d,g,h). In sample to13-5 and lm09-220 the S1 fabric is completely transposed into S2 (Figures 2e,f and 3b). Garnet grains appear as 400-600 μ m (radius) porphyroblasts overprinting the S1 and S2 fabrics (e.g. Figure 2g). Biotite porphyroblasts of \sim 500 μ m are either deformed by D2 (e.g. Figure 2b) or overprint the S1-S2 fabric (e.g. Figure 2d-f). Porphyroblasts were rotated during D3 (by different amounts depending on the sample) and incipient chlorite+white mica-bearing pressure shadows developed around biotite grains and at garnet rims (e.g. Figure 2d,g). At this stage, an S3 cleavage developed co-planar to S2, reactivating and folding the S2 fabric. Late euhedral grains of chlorite and white mica overprint all previous microstructures (especially in sample to13-5) and are oriented parallel to the microfold limbs associated to the S3-forming stage (e.g. Figure 2e and Airaghi et al., 2017a).

In all the metapelites, allanite grains form 100-500 μ m porphyroblasts subparallel to the S2 cleavage (Figure 3a), or cross-cut it (Figure 3b,c). No allanite grains were observed included in garnet. In samples to13-4 and to13-5, allanite has 10-15 μ m thick Th-rich rims (Figure 3a,b) and exhibits small (a few μ m in size) inclusions of quartz (\sim 90%) and white mica (\sim 10%, Figure 3a and Figure S1). In sample to13-7 allanite is surrounded by monazite and epidote (Figure 3c). Qualitative compositional maps show chemical homogeneity in REE-elements, U and Pb within the allanite grains (Figure S1).

The S1 and S2 fabrics are related to the prograde to peak metamorphic evolution (D1-D2 deformation stages in Figure 2a). Biotite and garnet are interpreted as index minerals that record the peak amphibolite-facies conditions (Figure 2a; Worley & Wilson, 1996; Airaghi et al., 2017a). In sample to13-5, biotite and garnet share sharp edges, suggesting that they grew

in chemical equilibrium. Microtextures suggest that garnet and biotite are post-S2 (post-D2) or, as in sample to13-4, biotite growth was possibly syn to post-D2. Due to its microtextural relationship with the S2 fabric, allanite is also linked to the peak metamorphic assemblage and is considered syn to post-S2. The chlorite+white mica intergrowths present at the biotite rims and the micrometric monazite at the allanite rims (in sample to13-7) appear related to the late metamorphic overprint under greenschist facies conditions, associated to the D3 deformation stage (Figure 2a).

The biotite porphyroblasts in samples to13-4 and to13-5 show an average X_{Mg} of 0.43-0.46 (Table 2), with variations at the proximity of cleavage-parallel cracks that formed syn- or post- the S2-forming stage and towards the rims (increase in X_{Mg} up to 0.51, Figure 5a). The Ti content in biotite porphyroblasts increases slightly from the core to the rims (0.08-0.14 pfu in to13-4, 0.07-0.09 for to13-5, Figure 5c).

Chemical heterogeneity is also observed in white mica. Compositional maps show that 10-15% of the white mica (muscovite is the major component) in the S2 cleavage in samples to13-4 and to13-7 has Si^{4+} of 3.2-3.25 (Figure 5b) and X_{Mg} of 0.54-0.61 (M_{SA} following Airaghi et al., 2017a). The remaining 80-85% of white mica, M_{SB} , is found in the S2 cleavage, contains a lower Si^{4+} of 3-3.15 and X_{Mg} of 0.43-0.6 (Figure 5b). Heterogeneous chemical composition is also observed in matrix muscovite of sample lm147, where the Si^{4+} varies from 3.1 to 3.3, for an X_{Mg} of 0.65-0.72, and K varies from 0.84 to 0.91 (Figure 5d).

3.3 | Crystalline basement

Samples lm09-52 and lm09-53 (from the Tonghua crystalline massif) are deformed metagranites; sample to13-12 is a deformed metagranodiorite (Figure 4). In all samples, the magmatic mineral assemblage of quartz+plagioclase+alkaline feldspar (+biotite in sample lm09-52) is overprinted by a greenschist mineral assemblage of albite+white mica+chlorite (+ actinolite+epidote in sample to13-12). In samples lm09-52 and lm09-53, white mica and chlorite have grown in zones of localized strain, indicated by the subgrain rotation and grainsize reduction of quartz. Both minerals also wrap feldspar and plagioclase grains and develop along micrometric-size fractures (Figure 4a). In sample to13-12, white mica grains form bands ~300 μm wide and are stretched along the main foliation. White mica-bearing layers alternate with albite-rich layers of few tens of micron wide (Figure 4b). In all samples, quartz exhibits undulatory extinction. Feldspar is strongly seriticed and often shows perthitic 'phantoms'. Allanite was only found in sample lm09-52 (20-80 μm ; Figure 4c). Grains are located in veins associated with titanite, apatite, biotite, xenotime (\pm monazite, \pm zircon) and greenschist-facies index minerals (chlorite and K-white mica; Figure 4c). Where allanite and titanite are in contact, the contact is irregular. Biotite generally shares sharp rims with titanite. Monazite and xenotime nucleated in rounded grains of 5-10 μm at allanite rims (Figure 4d). Point analyses and compositional maps reveal that white mica (dominant muscovite composition of 60-65%) is chemically homogeneous within each sample (Table 2). In sample lm09-52 muscovite has a Si^{4+} content of 3.18-3.22 pfu and X_{Mg} of 0.44-0.54 (Figure 5e). Muscovite in sample lm09-53 contains Si^{4+} of 3.2-3.3, but lower X_{Mg} of 0.36-0.46. Finally muscovite in sample to13-12 exhibits a higher Si^{4+} of 3.2-3.5 and X_{Mg} of 0.58-0.66. In sample lm09-52 and lm09-53 muscovite is associated with chlorite characterized by a Si^{4+} of 2.7-2.8 (pfu) for an X_{Mg} 0.44-0.6. The microstructural observations suggest that titanite and biotite are of magmatic origin, overprinted by the allanite growth which preceded the metamorphic monazite + white mica+chlorite greenschist assemblage.

3.4 | *P-T* framework

In the metasedimentary rocks, temperatures obtained from garnet-biotite thermometry for sample to13-5 range between 508 and $583 \pm 15^\circ\text{C}$ (Table 1). The temperatures from biotite-garnet core analysis pairs range between 508 ± 15 and $541 \pm 15^\circ\text{C}$, which are systematically lower than rim analysis pairs between 523 ± 15 and $583 \pm 15^\circ\text{C}$. Sample lm147, located far from the WF and in an upper structural level of the sedimentary series, yields an RSCM T_{peak} of $470 \pm 15^\circ\text{C}$ (Table 1).

In samples from the crystalline massif, multi-equilibrium thermobarometry constrains the greenschist-facies *P-T* conditions to 7 ± 1 kbar, $370 \pm 35^\circ\text{C}$ (see Figure S2). No chlorite was observed in sample to13-12; it was therefore not possible to directly calculate the pressure of muscovite growth. Results show that the greenschist overprint in the Tonghua crystalline massifs occurred at lower conditions than in its metasedimentary cover ($< 405^\circ\text{C}$), but at higher pressure conditions (> 6 kbar).

Our new thermometric estimates for these metasedimentary rocks are consistent with those of Airaghi et al. (2017a) that relate the composition of Ms_A in samples to13-4 and to13-7 to peak pressure conditions (11 ± 2 kbar, $530 \pm 20^\circ\text{C}$) and the composition of Ms_B to peak temperature conditions (6.5 ± 1 kbar, $575 \pm 10^\circ\text{C}$). The garnet-biotite bearing assemblages observed in sample to13-5 and lm09-220 suggest that they experienced peak metamorphic conditions similar to samples to13-4 and to13-7. Muscovite grains located in biotite pressure shadows and at biotite rims (Ms_C) in samples to13-4 and to13-7 are related to the greenschist-facies overprint at 4 ± 1 kbar, $380\text{--}450^\circ\text{C}$ (Airaghi et al., 2017a). Muscovite replacement therefore took place at the peak-*P*, peak-*T* and during the greenschist overprint by pseudomorphic replacement and dissolution-reprecipitation (Airaghi et al., 2017a and references therein).

4 | U-Pb/Th GEOCHRONOLOGY

4.1 | Methods

LA-ICP-MS U-Th/Pb dating of allanite was performed *in-situ* on the same polished thin sections used for the microstructural, petrological and thermobarometric studies (this study and Airaghi et al., 2017a). Allanite was analyzed at the Institute of Geological Sciences, University of Bern using a GeoLas Pro 193 nm ArF excimer laser ablation system coupled with an ELAN DRC-e quadrupole ICP-MS (full details are provided in Appendix S1). Isotope ratios were evaluated using the Th-isochron approach because the variability in U meant that the Terra-Wasserburg regression (Tera & Wasserburg, 1972) did not allow a regression line to be calculated precisely (e.g. Janots & Rubatto, 2014; Appendix S1). During the integration process, analyses exhibiting any age zoning were discarded. Therefore any potential effect of inclusions was identified and eliminated. The U-Pb and Th values obtained for allanite within each sample were therefore processed as a single population and used to calculate a single weighted mean age. This was in agreement with our petrological observations, which suggested only a single allanite growth stage within each sample.

4.2 | Results

Around 15 analyses were collected from each sample. Four grains of allanite were analyzed in metapelite to13-4 and meta-granite lm09-52, seven in metasedimentary sample to13-7 and three in metasedimentary sample to13-5. All analyzed allanite contains higher Th than U and highly variable initial Pb concentrations (Table S1). Within individual samples the U-Pb dates were concordant with Th-Pb dates, but were more dispersed and more significantly

affected by small variations in common Pb concentration (see Figure 6a,b for a comparison). We therefore used the Th-Pb dates for age interpretations.

Allanite in metapelites to13-4 and to13-5 yielded Th-Pb ages of 191.0 ± 9.6 Ma and 191.0 ± 22.0 respectively (Figure 6a,c). Sample lm09-220 yielded ages at 180.4 ± 6.4 Ma (Figure 6d). Allanite in sample to13-7 yielded ages of 201.0 ± 22.0 Ma (Figure 6e). Finally, allanite in sample lm09-52 (Tonghua crystalline massif) yielded ages at 176.0 ± 22.0 Ma, within the error of the metasedimentary cover ages (Figure 6f).

5 | $^{40}\text{Ar}/^{39}\text{Ar}$ CHRONOLOGY

5.1 | Methods

Metapelites to13-4, to13-5 and lm147 and Tonghua crystalline massif samples to13-12 and lm09-52 were selected for *in-situ* $^{40}\text{Ar}/^{39}\text{Ar}$ mica dating. Biotite and muscovite were analyzed *in-situ* by UV laser ablation and IR laser melting in polished 300 μm -thick sections to link ages to microstructural position. Samples were dated at The Open University, UK, following the procedure detailed in Appendix S1. One sample, to13-12, was analyzed at the University of Montpellier, France following the procedure described in Airaghi et al. (2017b). All Montpellier dates were recalculated using the decay constant and standard ages used for calculating dates obtained at The Open University (Appendix S1). Biotite and muscovite were analyzed in polished 300 μm -thick sections to link ages to microstructural position. Both *in-situ* infrared (IR) laser (melting) and *in-situ* ultraviolet laser (ablation) methods were used (Figure 7a-d; see below). Data are reported in Table S2. Age uncertainties are reported to 2σ ; uncertainties on the isotopic measurements are reported to 1σ .

5.2 | Results

The $^{40}\text{Ar}/^{39}\text{Ar}$ analyses are reported in Figures 7 and 8 and in Table S2. Biotite in sample to13-5 yielded UV laser $^{40}\text{Ar}/^{39}\text{Ar}$ dates ranging from 230 ± 17 Ma to 201 ± 7 Ma (the date with the largest uncertainty being at 233 ± 58 Ma) for grain cores and from 183 ± 12 Ma to 159 ± 10 Ma for grain rims (the majority of the analyses ranging between 183 ± 12 and 176 ± 13 Ma, Figure 7a,b). Ages yielded by IR-laser analyses range from 189.7 ± 1.2 Ma (mean biotite core) to 171.1 ± 1.4 Ma (mean biotite rim, white and black squares in Figure 7d). In sample to13-4 it was more difficult to spatially resolve the core and the rims age of biotite given the lower resolution of the IR-laser technique (Figure 7c). For this sample ages range from 215.5 ± 3.3 Ma to 187.6 ± 0.9 Ma (green circles in Figure 7d).

Muscovite of generation M_{SA} was not successfully dated since grains were too small and intergrown with chlorite, the analysis of which contaminated the Ar signal. The majority of the white mica grains stretched along the main S2 cleavage (M_{SB} in Figure 8a) in metapelite to13-4 yielded *in-situ* laser ablation ages ranging from 168 ± 9 Ma to 136 ± 7 Ma with four older ages ranging from 210 ± 22 to 173 ± 13 Ma (blue circles in Figure 8b). The spatial resolution of the ablation spot was not sufficient to distinguish between different core and rim ages. Three ages ranging between 130 ± 0.7 to 128 ± 0.8 Ma were yielded by IR laser melting in the same sample (see Table S2). The $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite dates obtained in the S2 cleavage of sample lm147 (Figure 8c) range from 159 ± 3 Ma to 150 ± 1 Ma (grey in Figure 8b). In the crystalline basement muscovite domains of samples lm09-52 and to13-12 (Figure 8d) yielded $^{40}\text{Ar}/^{39}\text{Ar}$ dates ranging from 141 ± 7 Ma to 122 ± 4 Ma and from 131 ± 17 Ma to 122 ± 4 Ma respectively (red and blue in Figure 8b).

6 | *P-T-t* INTERPRETATION

6.1 | Analytical uncertainty of the geochronological data

The Th-Pb ages obtained for allanite in the metasedimentary cover at different locations range between *c.* 223 Ma and 169 Ma (Late Triassic-Early Jurassic), but dates yielded by individual samples all overlap within error. U-Pb ages were concordant with Th-Pb ages for all analyzed samples. The age uncertainty mainly results from relatively high quantities of common Pb incorporated in the allanite grains. All allanite analyses exhibit a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio close to the 200 Ma reference value of 2.09 obtained from the ‘global lead evolution model’ of Stacey and Kramer (1975). The metasedimentary cover seems therefore to have experienced a consistent metamorphic history at the Late Triassic- Early Jurassic.

The core to rim variation in age uncertainty in biotite of sample to13-5 is independent of the intensity of the ^{40}Ar signal and different ages do not significantly overlap within the error. This is also the case for ages obtained for the same sample with the IR-technique. Despite the chemical heterogeneities of the mica grains, the *in-situ* infrared (IR) approach provides an independent check on the age measured with the UV *in-situ* approach.

The similarity between results obtained with the two extraction methods suggests that both extraction techniques sample the same age population(s). However, in the IR results some of the ‘bt core’ dates plot close to the ‘bt rim’ dates. This may be due to the lower spatial control, resulting in a potential mixing of Ar released from different age zones during laser melting. In sample to13-4 the spatial control of the IR-laser ablation was lower than in sample to13-5 and the zoning more patchy (see Figure 5a), resulting in indistinguishable ages between the core and the rims of biotite (green in Figure 7d). In this case all single biotite dates overlap within error. The probability distribution function (PDF) obtained for all biotite analyses clearly show two peaks at *c.* 220-210 and *c.* 180 Ma (Figure 7e), supporting the existence of two age populations.

In sample to13-4, no significant correlation is observed between the intensity of the ^{40}Ar signal and the dates, although the dates with the lowest uncertainties correspond to the ones with a ^{40}Ar signal > 0.04 V (Figure 8b; Table S2). Older ages do not overlap within error with muscovite ages clustering at *c.* 140 Ma. Data were also plotted in a $^{36}\text{Ar}/^{40}\text{Ar}$ vs $^{39}\text{Ar}/^{40}\text{Ar}$ and $^{40}\text{Ar}/^{39}\text{Ar}$ vs $^{38}\text{Ar}/^{39}\text{Ar}$ diagrams to potentially distinguish among different generations, but the plots were uninformative (full data are available in Table S2). In sample lm147 the ages of different grain sizes and associated chemical heterogeneities were too small to be differentiated with the spatial resolution of the laser, but their ages are consistent with the youngest muscovite ages in sample to13-4.

In the Tongva crystalline massif, allanite grains from sample lm09-52 yield ages of 198-154 Ma, within the uncertainty of the time interval yielded by both muscovite and allanite in the metasedimentary cover. Muscovite in the crystalline massif only preserves the youngest event (at *c.* 130 Ma) recorded in the sedimentary cover. The PDF of all muscovite dates (Figure 8e) shows that the majority of dates lie between 150 and 120 Ma (with the youngest contribution derived from analyses in the crystalline basement). There are also older contributions at *c.* 170 Ma and between 220 and 180 Ma.

6.2 | *P-T-t* path implications

The integration of new and previously acquired thermobarometric data with geochronological results provides major insights on the *P-T-t* path followed by the rocks of both the internal sedimentary cover and the basement in the central Longmen Shan (Figure 9a,b). The chemical homogeneity of allanite and its microstructural location aligned along the S2 cleavage, exhibiting S2-parallel inclusions (as in sample to13-4) or overprinting the S1-S2 (as in sample to13-5, see section 3.2) suggests that it grew during a single event either during or

after the S2 fabric-forming stage (syn to post-D2). Allanite growth may correlate with fluid pulses occurring along the prograde to peak path (Airaghi et al., 2017a), thus marking the attainment of pressure-peak or temperature-peak conditions (Figure 9a). However no allanite was observed included in garnet, suggesting that its growth postdates that of garnet (peak-*P*, Airaghi et al., 2017a), and is closer to the peak-*T* (Figure 9b). The allanite ages in sample lm09-220 show the smallest uncertainties and are likely to provide the best estimate for the timing of the peak-*T* (at 180 ± 6.4 Ma), assuming that allanite grew in the same time interval in different studied samples as suggested by microstructures.

Previous microstructural observations and thermobarometric estimates suggest that biotite started to grow prior to (or along with) garnet during the prograde path, but experienced a pulse of growth at the peak-*T*, where the majority of the large porphyroblasts developed (samples to13-4 and to13-7; Airaghi et al., 2017a; Figure 9a,b). The large interval of biotite growth is also supported by the fact that biotite is both deformed by D2 (to13-4) or overprints the S2-cleavage. The chemical heterogeneity of biotite may also be suggestive of long-lasting growth. Biotite $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained with both the *in-situ* laser ablation and IR laser techniques for sample to13-5 are in good agreement with IR laser biotite ages of sample to13-4 (Figure 7d). Biotite in both samples thus records the same metamorphic event. Furthermore, their ages also overlap the allanite ages. Despite peak temperatures > 550 °C (well above the closure temperature for Ar in biotite at ~ 280 °C, for a 100 μm biotite grain cooling at a rate of 1°C/Ma, Harrison, Duncan, & McDougall, 1985), $^{40}\text{Ar}/^{39}\text{Ar}$ ages in biotite grains seem therefore to have recorded the timing of their crystallization and to not have undergone significant loss of Ar by diffusion. The ability of biotite to retain Ar at > 500 °C has already been documented by Villa (2015) and might be extended here up to 580 °C. Biotite in amphibolite-facies rocks in the Himalayas also commonly record ages consistent with the timing of prograde growth (e.g. Stübner et al., 2017), although the older ages are commonly interpreted as being due to the presence of excess ^{40}Ar . The Ar inherited from the first biotite that grew during the prograde to peak metamorphic path in our samples may have contributed to the old ages. We cannot however exclude that biotite porphyroblasts might also have retained a part of the Ar signature of the early muscovite (M_{SA}) from which it partially developed – this has implications for the current understanding of Ar closure temperatures in biotite.

Muscovite in the S2 cleavage of samples to13-4 and to13-7 (M_{SB} in Figure 9a,b) chemically re-equilibrated at the peak-*T* (Airaghi et al., 2017a), but preserves older cores formed at peak-*P* conditions (M_{SA} in Figure 9a,b and section 3.2). The fact that muscovite relicts of the M_{SA} generation were smaller than the Ar laser spot may explain the variety of ages obtained for M_{SB} . In particular, a partial sampling of the M_{SA} may explain the spread of ages between 210-156 Ma (Figure 8e), the upper limit being similar to the ages recorded in the biotite core. Previous studies have shown that white mica grains (or parts of grains) that escaped chemical re-equilibration can also avoid Ar loss (Hames & Cheney 1997).

However, the majority of the *in-situ* UV $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite data from multiple samples and the ones with the lowest uncertainties in sample to13-4 yield much younger ages between 150-124 Ma (Figures 8b,e), younger than the ages yielded by biotite. Detailed petrological analysis of two areas of samples to13-4 and to13-7 reveals little late M_{SC} in the S2 cleavage (< 0.5 %), but rather only in porphyroblast pressure shadows. This might however not be representative of the all dated areas, where the percentage of the M_{SC} within the S2 might be variable.

In the samples from the Tonghua crystalline massif, the scarce preservation of the allanite-bearing assemblage makes it difficult to precisely assess the metamorphic conditions of allanite growth. However, no evidence of metamorphic conditions higher than the greenschist-facies (7 ± 1 kbar, 370 ± 35 °C, sample lm09-52) are observed. The Th-Pb allanite ages (sample lm09-52) constrain the timing of allanite growth at 176.0 ± 22.0 Ma. Muscovite records younger ages than allanite, in agreement with textural relationships (see section 3.2). In samples lm09-52 and to13-12 the $^{40}\text{Ar}/^{39}\text{Ar}$ dates obtained for muscovite in two different Ar laboratories are consistent at *c.* 140-130 Ma, supporting both the precision of the data and discarding the hypothesis of a constant mixing age. The existence of a single chemical population of muscovite also suggests that the mixing of different populations is unlikely. The estimated conditions for the greenschist metamorphism are consistent with the *P-T* conditions estimated for the growth of late muscovite and chlorite grains in the metasedimentary cover (M_{SC} in Figure 9a) (Airaghi et al., 2017a). The temperature estimated for the greenschist facies overprint (≤ 400 °C) is in this case below the nominal closure temperature of Ar in muscovite (425 °C for 100 μm radius grain and a cooling rate of 10 °C/Ma, Harrison, C  lerier, Aikman, Hermann, & Hizler, 2009) but close to its lower limit (405 °C, for the same conditions). We therefore relate $^{40}\text{Ar}/^{39}\text{Ar}$ dates to the crystallization of white mica between 140 and 120 Ma with some scatter due to ^{40}Ar contamination, low ^{40}Ar signal for some analyses (responsible for the ages with the largest uncertainties) and ^{40}Ar loss due to resetting, fluids or diffusion (responsible for the youngest ages). The greenschist-facies metamorphic event thus affected the Tonghua crystalline massif at 140-120 Ma.

Overall, the regional consistency of the $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 150-124 Ma (Figure 8e) corroborates the geological significance of the Early Cretaceous muscovite ages and discards the hypothesis of the presence of significant amount of excess ^{40}Ar into the analyzed minerals. We would expect ^{40}Ar contamination to vary on both the sample and grain scale. The integration of the petrological and geochronological results for the metasedimentary cover shows one major result: biotite seems to be able to retain crystallization ages at relatively high temperatures while the majority of the muscovite in the S2 cleavage does not. This difference might be (i) an effect of a protracted and slow cooling history, driving differences in Ar diffusion rates in muscovite and biotite characterized by a different grain size. At the temperatures experienced by the studied rocks, diffusion is generally considered to be one of main processes affecting the Ar concentration in the mica grain. Alternatively, the difference in biotite and muscovite ages may (ii) indicate different Ar crystallization and re-equilibration histories through the different metamorphic stages (D1, D2 and D3). In order to discriminate between hypotheses (i) and (ii) we tested different thermal scenarios in a series of simple Ar diffusion modelling experiments.

7 | DIFFUSION MODELLING

Two sets of cooling paths were tested (Figure 10): (1) simple cooling paths from 186 Ma (the most likely age of the thermal peak) and (2) more complex cooling paths constrained by independent geochronological and thermochronological data (see section 1; Kirby et al., 2002, Godard et al., 2009, Tan et al., 2017 and references therein). The MATLABTM-based program DiffArg (Wheeler, 1996, modified by Warren, Sherlock, & Kelley, 2011; Warren et al., 2012a and pers. comm) was used to determine whether there was a simple cooling scenario that best fitted the data. All model experiments were run for scenarios where temperature was decreased from a T_{peak} of 580 °C at 186 Ma (this study and Airaghi et al., 2017a), for a biotite grain radius of 0.5 mm and a muscovite grain radius of 0.05 mm (similar to that observed in thin section). In the model, the M_{SB} grains were considered homogeneous (without the M_{SA} inheritance) to predict the age of the only grains that completely re-

equilibrated at the peak- T at $c.$ 186 Ma, and check if it could approach the interval of 150-124 Ma. The pressure was assumed constant at 10 kbar as a first order approximation. The role of fluid in the Ar mobility is not considered in the model: it purely solves for thermally-activated diffusion.

The prograde path (from 530 to 580 °C, from 230 to 185 Ma; Figure 9b) was not modelled since at these temperatures it has already been shown by Ar diffusion models that no Ar is retained over geologically-meaningful timescales in an open system (Warren et al., 2011). The Ar diffusion model was therefore only run for the 186 Ma time period *after* the peak- T .

Following previous studies, the Crank-Nicholson solver was used, with a time integration step of 10 (Wheeler, 1996). A cylindrical diffusion geometry was assumed for both mica phases (Hames & Bowring, 1994), but with different diffusion lengths for muscovite and biotite (Wheeler, 1996 and references therein). The numerically-converged bulk age was calculated following the method outlined in Warren et al. (2012a).

We tested a series of models with simple cooling paths, with temperature decreasing linearly at rates of 2, 15 and 30 °C/Ma respectively (P1, P2 and P3 in Table 3 and Figure 10a) to understand the behaviour of the Ar record for different thermal histories. Following other thermochronology constraints from the literature –mainly obtained for the crystalline massifs and covering the last 30 Ma– we also explored two more complex synthetic temperature paths (path A and B in Table 3 and Figure 10b) where temperature decreases linearly between the different T - t segments. In path A, temperature decreases from 580 to 400 °C at 4 °C/Ma (constrained by this study's results for the Tonghua massif) and from 400 to 0 °C at 2.8 °C/Ma such that 0°C is reached after 186 Ma model time (constant cooling as suggested by Roger et al., 2011). In path B, temperature decreases from 580 to 400 °C at 4 °C/Ma as above, then from 400 to 200 °C at 1.5 °C/Ma (based on the fission track and U-Th/He ages of Kirby et al., 2002, Godard et al., 2009, Tan et al., 2017) and subsequently cools to reach 0 °C after 186 Ma model time (Table 3).

The best-fit model solutions were initially investigated for biotite, with the resulting model then tested on muscovite. All models were run for open system scenarios. Core and rim ages (50-100 μ m from the rim in the analyzed samples) were used to test the fit of the model rim age predictions. Model uncertainties are described in detail in Mottram, Warren, Halton, Kelley, and Harris (2015). In summary, the experimentally-derived diffusion parameters provide the greatest source of uncertainty, and in these models would shift the resulting bulk age \pm 4 Ma.

The predicted model ages for biotite that cooled from 580 to 0 °C at 2, 15 and 30 °C/Ma (models P1, P2 and P3) are 58, 171 and 177 Ma respectively (Figure 10a). The bulk ages predicted for biotite cooling along path A are 131 Ma, whereas those for path B are 110 Ma. Muscovite models predicted ages of 93, 175 and 181 Ma for the paths P1, P2 and P3 respectively (Figure 10a), and 140 Ma and 133 Ma for open system paths A and B respectively (Figure 10b).

8 | DISCUSSION

8.1 | Different Ar histories for biotite and muscovite

In all model experiments, regardless of the rate at which the system cooled, predicted biotite ages were significantly younger than the measured ones, as expected when following the closure temperature formulation (Figure 10a,b). Constant cooling rates higher than 30 °C/Ma (P3) are unlikely for the area, since they would imply that metasedimentary units reached the surface by 165 Ma, in contrast with previously published thermochronological data. It was instead possible to approach the measured age on muscovite at 150-124 Ma with models experiments performed along the T - t paths A and B. However, the fact that the mica ages are

uniform among different samples (and over 200 km) suggests that these highly contrived open system models should be invoked for all samples experiencing relatively high temperatures ($> 500\text{ }^{\circ}\text{C}$), and therefore also for biotite. Nevertheless, these models are completely unable to account for the difference between biotite and muscovite ages. This suggests that the age differences between biotite and mica cannot be ascribed to diffusion due to slow cooling in minerals with different grain sizes and strengthen the hypothesis that biotite and muscovite experienced different growth and re-setting histories that affected the Ar concentration in different ways, as strongly suggested by petrological observations. In particular, the age difference may indicate that (i) the system remained opened to Ar for muscovite in the S2 cleavage longer than for biotite porphyroblasts, until the temperature-deformation-fluid conditions were no able to promote Ar resetting and/or that (ii) muscovite in the S2 cleavage experienced a post peak- T crystallization event (growth of Ms_C) that biotite did not experience, leading to the partial resetting of the Ar system.

8.2 | Role of microstructural position and replacement reactions on $^{40}\text{Ar}/^{39}\text{Ar}$ ages

From a petrological and microstructural point of view, the age difference between biotite and muscovite for the $^{40}\text{Ar}/^{39}\text{Ar}$ system might have been favored by different factors:

(1) *Different microtextural sites for biotite and muscovite.* Several studies have shown that deformation can act as a network for inter-grain loss of radiogenic ^{40}Ar (Kramar, Cosca, & Hunziker, 2001; Mulch, Cosca, & Handy, 2002; Cossette, Schneider, Warren, & Grasemann, 2015). The elongated muscovite forming the main S2 cleavage was likely to have preferentially accommodated the post peak- T deformation over the large porphyroblasts of biotite, preventing extensive ^{40}Ar re-equilibration in biotite.

(2) *Fluid-driven replacement of Ms_B by Ms_C .* Petrological analyses show a compositional variability in muscovite of these samples (see section 3 and Figure 5). Although Ms_C is not the major constituent of the S2 cleavage in the thin section areas that we studied in detail, its percentage might vary within the sample and within the analyzed areas. Furthermore, the laser spot size used during the $^{40}\text{Ar}/^{39}\text{Ar}$ analyses was, on average, larger than the spatial scale of the muscovite chemical heterogeneity. The ages of muscovite in the S2 cleavage might therefore represent a mixture between two end-members with the oldest ages approaching the age of growth of Ms_A and the youngest ages approaching the crystallization ages of Ms_C . It has already been documented that white mica can preserve crystallization ages at least up to 500°C , depending on the length of time the rock experienced those temperatures and the openness of the grain boundary system (Warren et al, 2012a; Villa, 2015). The occurrence of a re-crystallization (or muscovite replacement) event at 150-124 Ma instead of simple cooling is also supported by the fact that the sample in an upper structural position (lm147) seems to record only the youngest event and that the muscovite generation observed in the Tonghua crystalline massif grew in the same time interval.

(3) *Acquired intra-grain porosity in muscovite.* Petrological results show that while Ms_B partially re-equilibrated at the peak- T (except relicts of Ms_A peak muscovite), biotite porphyroblasts never experienced re-crystallization after their growth at the peak- T . While muscovite recrystallization during metamorphism is a more efficient mechanism for Ar resetting than diffusion (Villa, 1998; Allaz et al. 2011, McDonald et al., 2016), the absence of recrystallization in biotite may instead preserve crystallization ages (Kelley, 1988; Di Vincenzo et al., 2001; Villa, 2016). The intra-grain porosity of newly crystallized biotite grains is likely to be lower than the intra-grain porosity of muscovite grains partially replaced during the P - T path by ‘pseudomorphic replacement’ (Putnis, 2009; Putnis & Timm, 2010; Airaghi et al., 2017a). This would significantly decrease the potential for ^{40}Ar escape from

biotite and from relicts of M_{SA} shielded from successive re-equilibration due to their microstructural position. On the other hand, the acquired porosity of muscovite of M_{SB} composition, coupled with fluid-driven dissolution-reprecipitation process as indicated by the chemical heterogeneity, may have favored the escape of ^{40}Ar .

Several studies stress the importance of the availability of water for facilitating the resetting of the isotope record (Di Vincenzo et al. 2001; Villa, 2010; Berger, Wehrens, Lanari, Zwingmann, & Herwegh, 2017). The range of $^{40}\text{Ar}/^{39}\text{Ar}$ ages in sample to13-4 suggests that there was significant variability in the fluid availability and permeability during the metamorphic cycle –otherwise all minerals should record a narrow range of exhumation-related ages following the thermal peak (Warren et al., 2012b). At the scale of the mineral assemblage, three successive fluid release events were responsible for successive muscovite chemical re-equilibration during the prograde path in sample to13-4 (Airaghi et al., 2017a). Three intervals were also recognized in our geochronological dataset for samples of the to13 series, defined by (1) the biotite core and M_{SA} ages, (2) the biotite rims and M_{SB} ages and (3) the M_{SC} ages at *c.* 140-130 Ma. Mineral geochronometers might therefore be viewed as ‘geohygrometers’ that essentially date fluid circulation episodes (often related to mineral re-equilibration events; Villa et al., 2010).

The chemical and geochronological heterogeneity of mica in different microstructural sites indicates that in our samples the Ar record is mainly controlled by the rates of fluid-driven dissolution-reprecipitation processes rather than diffusion, as has already been suggested in lower grade metamorphic rocks (e.g. Mulch & Cosca, 2004; Villa et al., 2014; Cosette et al., 2015). The microstructural position of the grains might also be a key factor in explaining the different behavior of Ar between muscovite and biotite.

While biotite (and garnet) indicate a precise and relatively limited part of the metamorphic path (prograde to peak amphibolite-facies metamorphism at 220-180 Ma), the matrix muscovite seems to record a large part of the metamorphic history between 220 and 124 Ma (post peak-*P*), providing an age interval for each stage of the metamorphic path recorded in the chemistry of the mineral assemblage. Ages in the range of 150-124 Ma are therefore likely to represent the timing of a post peak-*T* metamorphic stage during decompression, down to the greenschist facies conditions.

8.3 | Regional tectonic implications

The allanite and biotite ages (200-170 Ma) are consistent with other data constraining the onset of the amphibolite-facies metamorphism in the Danba area (~ 200 km southeastward, Huang et al., 2003; Weller et al., 2013; Jolivet et al., 2015) and with muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ ages in the Northern Longmen Shan (Yan et al., 2011). Our ages are also in agreement with the time interval proposed for the emplacement of Mesozoic granites in the Songpan-Ganze region (Roger et al., 2004; de Sigoyer et al., 2014), which may mark the thermal peak in the westernmost Songpan-Ganze sedimentary series (Figure 11). In detail, $^{40}\text{Ar}/^{39}\text{Ar}$ ages in biotite record two-stages of crystallization during amphibolite-facies metamorphism (*c.* 220-200 Ma and *c.* 180 Ma), the timing of which is consistent with the age interval of the allanite analyzed in this study (Figure 11).

On the basis of petrological observations, geochronological results and diffusion modelling we relate the Late Triassic- Early Jurassic Th-Pb allanite age to a medium-grade metamorphic event at amphibolite-facies conditions in the Songpan-Ganze units of the central Longmen Shan syn- to post- the S2-forming phase of deformation. This medium-*T* metamorphic period lasted for over 20 Ma (Figure 11).

The allanite ages in the Tonghua massif may indicate that this slice of basement was already (marginally) affected by metamorphism (and deformation) during the Early Jurassic, although they might also be compatible with the upper limit of the time range indicated by the $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite ages. The $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite ages show indeed that the major re-activation of the massif occurred in the Early Cretaceous (Figure 11). The ages are unlikely to represent mixing ages between a Late Triassic- Early Jurassic (200-180 Ma) metamorphic event and a much younger Cenozoic event since first, there is no evidence of Cenozoic ages related to metamorphism in the central Longmen Shan, and second the ages recorded in the sedimentary cover are also recorded in the Tonghua crystalline massif. Furthermore, Early Cretaceous ages were obtained also in the Pengguan crystalline massif (40 km southeastwards, Figure 11), where there is no evidence of Late Triassic- Early Jurassic metamorphism (Airaghi et al., 2017b).

In the internal metasedimentary cover, the occurrence of a greenschist-facies event during the Early Cretaceous is consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ ages recorded in the Wenchuan fault zone (119-114 Ma, Arne et al., 1997) and with 123-120 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ biotite ages from the Danba area (Xu et al., 2008). The Early Cretaceous also marks a change in the type and rate of sedimentation of the autochthonous units in the western Sichuan basin, that become characteristic of a flexural basin forming in response to a rapid uplift of the belt (Liao, Hu, Zhang, Chen, & Sun, 2009). In order to explain the decreasing age of the Early Cretaceous event approaching the front of the belt we propose that the related deformation phase firstly affected sediments in the North-West of the Tonghua area (Im147) at 160-147 Ma, and then propagated to the South-East at 150-135 Ma (to13-4), and to the basement in the Tonghua and Pengguan crystalline massifs at 140-118 Ma (Im09-52) and 145-130 Ma respectively (Figure 11).

Note that the Early Cretaceous phase is so far undocumented in the metamorphic evolution of the belt (except in the studies of Airaghi et al., 2017b) and marks the onset of thick-skinned deformation in the Longmen Shan. At this time the internal units were already highly thickened (~30 km; Airaghi et al., 2017a) and difficult to deform without propagating the deformation towards the front of the belt. Furthermore, our petrochronological results show that metasedimentary units in the internal part of the Longmen Shan were already partially exhumed by the Early Cretaceous, well before the Cenozoic exhumation phase.

The combination of petrological data with mica and allanite ages enable the first order thermal history for the internal sedimentary units of the Longmen Shan to be documented, and associated with different phases of re-activation (Figure 12). The Early Cretaceous muscovite ages appear to be associated with a late greenschist overprint at ~320-400 °C. The prograde path is constrained from petrology (Airaghi et al., 2017a) while the $T-t$ estimates for the Miocene are derived from low- T thermochronology (Kirby et al., 2002; Godard et al., 2009; Wang et al., 2012) and from previously published $^{40}\text{Ar}/^{39}\text{Ar}$ (Airaghi et al., 2017b). The cooling path obtained for the internal sedimentary units (red in Figure 12) includes a relatively fast cooling rate of 4.5 ± 0.5 °C/Ma from 580 °C to ~400 °C between 185 and 140 Ma (Early Cretaceous). This phase was followed by slower cooling at ~ 1.5 °C/Ma until the Cenozoic exhumation phase at *c.* 20-10 Ma (Figure 12). The cooling rate of the internal Tonghua crystalline massif between 140 and 10 Ma was calculated at 1.4 ± 0.3 °C/Ma by the integration of our geochronological results and recent zircon fission track ages revealing a rapid exhumation of the massif from ~ 200 °C in the last 10 Ma (Tan et al., 2017).

In the Tonghua massif, the $P-T$ data related to the Jurassic event are not precisely constrained. However the absence of evidence for metamorphism higher than greenschist facies suggests that the Tonghua massif experienced conditions similar to those estimated for the Early Cretaceous event. The shape of cooling path of Figure 12 is similar to the one proposed for Danba region (grey lines in Figure 12; Huang et al., 2003), but in that area, the

Early Cretaceous event remains unrecognized. We also observe a convergence of the thermal histories of the sedimentary units and crystalline massifs at 140-138 Ma. The basement and the sedimentary cover seem therefore to have experienced a coherent exhumation history since the Early Cretaceous re-activation. The crystalline massifs and the sedimentary cover experienced different thermal histories prior to the Early Cretaceous. The medium grade metamorphic conditions recorded only in the metasedimentary cover at 200-180 Ma suggest that it thickened independently from the basement. A major decollement between the sediments and the basement was therefore active during the Triassic- Early Jurassic.

Together these observations suggest that both the central Longmen Shan and the Danba region experienced a similar thermal evolution, although in the Danba region the Early Cretaceous re-activation has thus far not been documented. In detail, the lower peak temperatures recorded in the studied area result in slower cooling rates during Cretaceous to Cenozoic times in the central Longmen Shan relative to the Danba area. The Early Cretaceous re-activation in the central Longmen Shan may be due to the far field effects of the collision between the Lhasa and Qiangtang blocks in the central Tibet, as suggested by Airaghi et al. (2017b) and references therein.

9 | CONCLUSIONS

This study demonstrates the complexity of interpreting $^{40}\text{Ar}/^{39}\text{Ar}$ ages of low to medium grade metamorphic rocks, especially for matrix phyllosilicates. The combination of petrological and geochronological results shows that in Longmen Shan, biotite porphyroblasts in amphibolite-facies metapelites retain crystallization ages (i.e. ages that are consistent with U-Th/Pb allanite ages), despite experiencing relatively high temperatures (~580 °C). Muscovite in the main foliation that re-equilibrated at the peak- P , peak- T , and during the greenschist-facies overprint instead records a more complex $^{40}\text{Ar}/^{39}\text{Ar}$ story. The muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ ages comprise a mixture derived from the partial sampling of early M_{SA} relicts and a regionally consistent signal at *c.* 140-130 Ma. The difference between biotite and muscovite ages is not explainable by simple diffusion during protracted and slow cooling for grains of different size, as revealed by diffusion modelling experiments. Such a difference instead suggests successive re-crystallization events. The microstructural position of muscovite in the main foliation as well as the acquired porosity during the previous metamorphic history may also have favored the resetting of the Ar concentration in muscovite.

The combination of different petrological and geochronological methods provides an interpretative framework for the $^{40}\text{Ar}/^{39}\text{Ar}$ ages. Despite the fact that the *in-situ* UV analyses could not resolve all the chemical heterogeneities due to their small size, the coupling with detailed petrological studies allowed the different generations of mica to be matched to their $^{40}\text{Ar}/^{39}\text{Ar}$ signature. *In-situ* $^{40}\text{Ar}/^{39}\text{Ar}$ dating is a powerful technique that allows the entire metamorphic history to be traced by bracketing in time the different stages.

By using both Ar diffusion modelling and petrological observations, this study also tests all the hypotheses that may explain the $^{40}\text{Ar}/^{39}\text{Ar}$ ages. Here we show robust evidence for petrological and microstructural processes prevailing over thermally-driven diffusion even at high temperatures. The complexity of the studied samples required significant underlying assumptions but the regional consistency of the data strengthen the geological interpretation of our results.

The $^{40}\text{Ar}/^{39}\text{Ar}$ biotite and U-Th/Pb allanite ages constrain the timing of medium-grade metamorphism in the sedimentary units in the central Longmen Shan (Tonghua area) to 220-180 Ma. The $^{40}\text{Ar}/^{39}\text{Ar}$ ages of muscovite in the S2 cleavage constrain the timing of the post- T peak metamorphism up to the metamorphic overprint at greenschist facies conditions to 140-130 Ma. This event is also recorded in the crystalline Tonghua massif and is associated with deformation and a greenschist-facies overprint at 7 ± 1 kbar, 370 ± 35 °C. Our results show that metamorphism and deformation affected the sedimentary cover of the internal Longmen Shan (and maybe marginally the South China basement in the Tonghua crystalline massif) during the Late Triassic-Early Jurassic. This event was followed by a previously poorly-recorded Early Cretaceous re-activation event that was responsible for the partial exhumation of the medium-grade metamorphic rocks and the crystalline massifs as a coherent system. This study therefore shows that an important part of the crustal thickening and exhumation in eastern Tibet is inherited from the complex Mesozoic history, thus preceding the Cenozoic re-activation. The basement (in the crystalline massifs) was actively involved in the deformation since the Early Cretaceous.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Appendix S1. Analytical methods for geochronology

Figure S1. Compositional X-ray maps of allanite of metapelites to13-4 and to13-7.

Figure S2. Thermobarometric estimates for samples lm09-52 and lm09-53 from the Tonghua crystalline massif obtained with the white mica-chlorite-quartz multi-equilibrium approach.

Table S1. Chemical analyses for allanite of two representative metapelites: samples to13-5 and to13-4.

Table S2. Ar data for all analyzed samples.

FIGURE CAPTIONS

Figure 1 (a) Simplified geological and structural maps of eastern Tibet, modified from Billerot et al. (2017). The inset indicates the location of the Longmen Shan within Asia. Xb = Xuelongbao Massif, P = Pengguan Massif, WF = Fault, BF = Beichuan Fault, GF = Guanxian Fault. (b) Geological map of the studied area. Sample locations are indicated by red dots. The black line defines the profile of the cross section in panel c. (c) Geological cross section along the profile AA'. The location of the studied samples is projected on the section (red dots).

Figure 2 Photomicrographs of studied metapelites. Mineral abbreviations are from Whitney and Evans (2010) except for white mica = Wm. (a) Interpretative sketch of the microstructural and mineral evolution of the studied samples. (b) Plane polarized light (PPL) image of deformed biotite porphyroblast and the S1 and S2 Wm-bearing cleavage (red and blue) in sample to13-4. At biotite rims Wm + Chl develop (dashed green line). (c) Backscatter (BSE) image showing the geometric relations between the crenulated S1 Chl + Wm cleavage (red) and the S2 Wm-bearing cleavages (with minor chlorite, blue) in sample to13-4. (d) BSE image of a biotite porphyroblast in sample to13-4 with its incipient Wm + Chl pressure shadows (dashed green lines), modified from Airaghi et al. (2017a). (e) PPL image of biotite porphyroblasts in sample to13-5 overgrowing the main cleavage. Late, narrow white mica flakes superimpose the biotite grain. (f) BSE image of garnet and biotite porphyroblasts in sample to13-5. (g) BSE image of garnet in sample to13-7, recording both S1 and S2 in inclusion trails. (h) PPL image of sample lm147. The deformed porphyroclast is made of Qz + Fe-oxide (pseudomorphing an early allochthonous clast). The inset shows an enlarged view of the S1 cleavage (red) preserved within S2 domains (underlined in blue).

Figure 3 (a) BSE image of allanite porphyroblasts aligned with, and partly overgrowing, the S2 cleavage (blue dashed line) in sample to13-4. (b) Allanite overgrowing the main cleavage in sample to13-5. (c) BSE image of allanite grains overprinting the S1-S2 cleavage in sample to13-7. Allanite is surrounded by a Mnz+Ep rims as shown in the enlarged view on the right.

Figure 4 Samples from the Tonghua crystalline massif. (a) PPL image of the white mica-bearing domains grown in deformed metagranite lm09-52. (b) BSE image of the white mica-bearing cleavage in deformed metagranodiorite to13-12. Red contours limit the amphibole grains. (c) PPL image of Chl+Wm+Aln-bearing greenschist veins (GS) in metagranite lm09-52. (d) BSE image of mineral phases associated with Aln in sample lm09-52.

Figure 5 Quantitative compositional X-ray maps. (a) X_{Mg} ($Mg^{2+}/(Mg^{2+}+Fe^{2+})$) in biotite in sample to13-4. (b) Si^{4+} content of muscovite in the S1 and S2 cleavage of sample to13-4 (modified from Airaghi et al., 2017a). (c) Ti (pfu) content of biotite in sample to13-5. (d) Si^{4+} content of muscovite in the main cleavage of sample lm147. The saturated red region corresponds to extremely small Qtz-rich cracks. (e) Si^{4+} (apfu) in muscovite in sample lm09-52.

Figure 6 Th-Pb allanite ages (a, c, d, e and f). Each ellipse represents one analysis. Initial values of common $^{208}Pb/^{206}Pb_c$ are indicated in brackets below the age in the yellow frames. Panel (b) is an example of Tera-Wasserburg diagram for sample to13-4.

Figure 7 $^{40}Ar/^{39}Ar$ results for biotite in samples to13-5 and to13-4. (a) Reflected light image of a biotite grain in sample to13-5. Representative locations of laser spots are indicated by circles. (b) $^{40}Ar/^{39}Ar$ ages for biotite core (black) and rims (white) obtained with the *in-situ* UV ablation technique for sample to13-5. Analyses are shown plotted from young to old. (c) Reflected light image of analyzed biotite grains in sample to13-4. (d) IR-laser $^{40}Ar/^{39}Ar$ ages for biotite core (black) and rims (white) for sample to13-5 and to13-4 (green circles) obtained with the *in-situ* IR single grain fusion technique. (e) Probability distribution function (PDF) of all biotite ages obtained for 10000 random iterations (Monte-Carlo approach) generated from the age and uncertainties measured values.

Figure 8 $^{40}Ar/^{39}Ar$ results for white mica in samples to13-4, lm147, lm09-52 and to13-12. Dashed yellow lines limit the domains dated by $^{40}Ar/^{39}Ar$. (a) Analyzed S2-forming white mica (yellow) in sample to13-4. (b) *In-situ* UV (to13-4, lm09-52 and to13-12) and IR (lm147) $^{40}Ar/^{39}Ar$ ages for all analyzed white mica with relative errors. Analyses are shown plotted from young to old. WF = Wenchuan Fault. (c) Analyzed muscovite in sample lm147. (d) Analyzed white mica domains in meta-granite lm09-52. Laser spots are indicated by circles. One analysis (white dashed line) includes two spots. (e) Probability distribution function for all white mica ages (generated as in Figure 7).

Figure 9 Estimated *P-T-t* path for the internal metasedimentary units from petrological and geochronological constraints (see text for details). Tonghua M= Tonghua crystalline massif. The age of M_{SB} is not directly measured but deduced from *P-T* relations and allanite ages (see text). The rapid *T-t* variation in the last 10 Ma in panel (b) is constrained by apatite and zircon fission track thermochronology and (U-Th-He) data collected in the crystalline massifs (Kirby et al. 2002; Wang et al., 2012; Tan et al., 2017 and references therein and in the text). Time is from 250 Ma ago to present (left to right).

Figure 10 Results of Ar diffusion modelling experiment for biotite (radius 0.5 mm) and muscovite grains (radius 0.05 mm) for cooling paths P1, P2, P3 in an open system (a), for path A and B in an open system (b). Time is 'model time', which means that 0 = time of the temperature peak and 186 Ma = present day. The left diagrams are the modelled temperature paths; middle diagrams represent the variation of the age integrated over the grain distance

(bulk age) with time; right diagrams are the core to rim age variation within a single biotite grain. Grey box: range of Th-Pb allanite ages.

Figure 11 Summary of *in-situ* geochronological results and related metamorphic and tectonic events. * = age reported in Airaghi et al. (2017b) for the greenschist metamorphism in the Pengguan massif. Schematic cross sections are modified from Airaghi et al. (2017a). Red: metasedimentary cover. Blue: South China block (including the crystalline basement). The yellow frame indicates the time range for the emplacement of the Mesozoic granites (from Roger et al., 2004; de Sigoyer et al., 2014 and references therein).

Figure 12 Cooling histories for internal sedimentary units (red), internal Tonghua crystalline massif (black) and external crystalline Pengguan massif (green). Coloured rectangles represent the estimated temperature conditions at each stage (from petrology). Numbers between the squares are deduced cooling rates in °C/Ma. The red dashed cooling rate is the one that also appears in path B for Ar diffusion modelling. *T-t* estimates for the Pengguan massif are from $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite ages (Airaghi et al., 2017b); *T-t* estimates for the Tonghua massif at 10 Ma are from zircon fission track (Tan et al., 2017); *T-t* estimates for the Pengguan massif at < 20 Ma are from zircon He ages (Godard et al., 2009). Grey lines are the cooling rates for the Danba units (~ 200 km southeast of the Longmen Shan) by Huang et al. (2003). Yellow frame: interval of granite emplacement in the Songpan-Garze block. D1, D2, D3 refer to the different deformation phases described in section 3.2 and in Figure 2a. The timing of D4 is restrained to Cenozoic pulses of exhumation identified by low-*T* thermochronology.

Table 1 Location and physical conditions of the samples. RSCM: Raman Spectroscopy on Carbonaceous Material. ^a: data from Airaghi et al. (2017a).

Table 2 Representative chemical analyses for samples to13-5, lm09-52, lm09-53 and to13-12. Chemistry of samples to31-4 and to13-7 is described in details by Airaghi et al. (2017a).

Table 3 *T-t* paths tested in Ar diffusion modelling experiments. Model time is the time passed from the temperature peak stage, where *t* = 186 Ma is the present day.

Table 1 Location and physical conditions of the samples. RSCM: Raman Spectroscopy on Carbonaceous Material. ^a: data from Airaghi et al. (2017a).

Sample name	Long	Lat	Lithology	T _{peak} conditions (°C)	Method used
to13-4	E103.6823	N31.7205	Garnet-biotite schist	575 ± 10 ^a	Phase diagrams, Grt-Bt thermometry ^a
to13-7	E103.6801	N31.7292	Garnet-biotite schist	576 ± 10 ^a	Phase diagrams, Grt-Bt thermometry ^a
to13-5	E103.681183	N31.725037	Garnet-biotite schist	508-583 ± 15	Grt-Bt thermometry
lm09-220	E103.710983	N31.749128	Garnet-biotite schist	n.a.	n.a.
lm147	E103.722970	N31.824930	Biotite-white mica schists	470 ± 15	RSCM
lm09-52	E103.728857	N31.605644	metagranite in greenschist facies conditions	370 ± 35	Chl-Wm multi-equilibrium
lm09-53	E103.730032	N31.602583	metagranite in greenschist facies conditions	370 ± 35	Chl-Wm multi-equilibrium
to13-12	E103.731531	N31.599619	metadiorite in greenschist facies conditions	370 ± 35	Chl-Wm multi-equilibrium

Table 2 Representative chemical analyses for samples to13-5, lm09-52, lm09-53 and To13-12. Chemistry of samples to31-4 and to13-7 is described in details by Airaghi et al. (2017a)

Sample	TO13-4 TO13-5				LM147	lm09-53		lm09-52		To13-12
Mineral	Bt	Bt	Grt core	Grt rim	Ms	Ms	Chl	Ms	Chl	Ms
SiO ₂	36.48	35.55	36.23	34.79	47.97	48.94	26.22	47.56	26.88	49.51
TiO ₂	1.33	1.48	0.05	0.04	0.399	0.63	0.06	1.57	0.04	0.08
Al ₂ O ₃	19.23	18.99	21.39	20.22	32.30	25.23	19.06	28.34	21.38	27.45
FeO	20.20	20.78	32.91	35.98	1.33	9.68	30.48	4.01	25.29	5.07
MnO	0.01	0.00	2.97	1.12	0	0.09	0.79	0.02	0.41	0.01
MgO	9.35	9.20	1.60	1.82	1.628	3.80	13.45	2.09	16.68	4.24
CaO	0.00	0.00	4.33	3.48	0.02	0.06	0.03	1.21	0.01	0.02
Na ₂ O	0.27	0.22	0.02	0.05	0.37	0.10	0.05	0.20	0.02	0.12
K ₂ O	8.28	7.61	0.01	0.05	10.07	10.25	0.07	10.28	0.04	8.72
Total	95.15	93.83	99.51	97.54	94.08	98.78	90.20	95.28	90.76	95.20
Cations (pfu)										
Si	2.76	2.611	2.82	2.79	3.22	3.28	2.77	3.22	2.72	3.32
Ti	0.08	0.082	0.00	0.00	0.02	0.03	0.00	0.08	0.00	0.00
Al	1.72	1.645	1.96	1.91	2.55	1.99	2.37	2.27	2.55	2.17
Fe ⁺²	1.28	1.277	2.14	2.41	0.07	0.54	2.69	0.23	2.14	0.28
Mn	0.00	0.000	0.20	0.08	0.00	0.01	0.07	0.00	0.04	0.00
Mg	1.05	1.007	0.19	0.22	0.16	0.38	2.12	0.21	2.52	0.42
Ca	0.00	0.000	0.36	0.30	0.00	0.00	0.00	0.09	0.00	0.00
Na	0.04	0.032	0.00	0.01	0.05	0.01	0.01	0.03	0.00	0.02
K	0.80	0.713	0.00	0.00	0.86	0.88	0.01	0.89	0.01	0.75
Oxygens	11	11	12	12	11	11	14	11	14	11
XMg	0.45	0.44	0.08	0.08	0.69	0.41	0.44	0.48	0.54	0.60

Table 3 T-t paths tested in Ar diffusion modeling experiments. Model time is the time passed from the T-peak stage, where t= 186 Ma is the present day.

Path	T _{peak} (°C)	model time (Ma)	T (°C)	T decrease
P1	580	186	208	linear
P2	580	39	0	linear
P3	580	19.9	0	linear
A	580	45	400	linear
		186	0	linear
B	580	45	400	linear
		175	200	linear
		186	0	linear























